

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
17 November 2005 (17.11.2005)

PCT

(10) International Publication Number
WO 2005/108298 A1

(51) International Patent Classification⁷: **C01G 21/20**,
H01M 4/56, 10/12, 4/20

(21) International Application Number:
PCT/IB2005/002373

(22) International Filing Date: 18 March 2005 (18.03.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/803,491 19 March 2004 (19.03.2004) US

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
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TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA,
ZM, ZW.

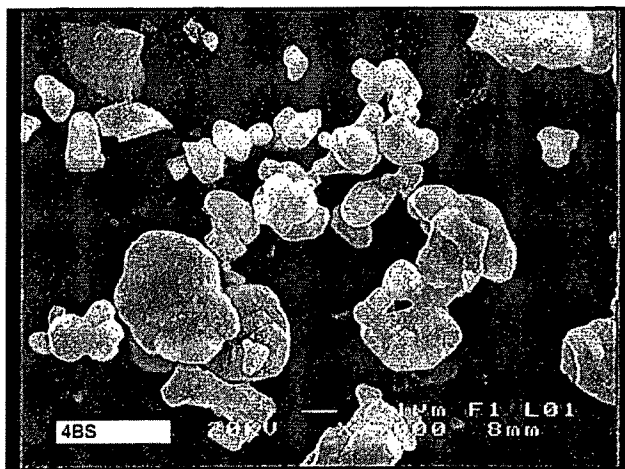
(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO,
SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN,
GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: PRODUCTION OF TETRABASIC LEAD SULFATE FROM SOLID STATE REACTIONS FOR THE PREPARATION
OF ACTIVE PLATES TO BE USED IN LEAD-ACID BATTERIES



(57) Abstract: The production of tetrabasic
lead sulfate by means of solid state reactions
at high temperatures allows the formation of
powders having particle sizes of less than 10
µm. A chemical reaction takes place between
lead oxide and a sulfated compound in a single
high temperature treatment.

PRODUCTION OF TETRABASIC LEAD SULFATE FROM SOLID STATE REACTIONS FOR THE PREPARATION OF ACTIVE PLATES TO BE USED IN LEAD-ACID BATTERIES

CROSS-REFERENCE TO RELATED PATENT APPLICATIONS

[0001] This application claims the benefit of U.S. Patent Application No. 10/803,491, filed March 19, 2004. The entire disclosure of U.S. Patent Application No. 10/803,491 is incorporated by reference herein.

FIELD OF THE INVENTION

[0002] This invention relates generally to the production of tetrabasic lead sulfate and more specifically to the production of tetrabasic lead sulfate from solid state reactions for the preparation of active plates to be used in lead-acid batteries.

BACKGROUND

[0003] The preparation of active electrodes or plates for lead-acid batteries involves three steps: a) paste application to a supporting grid, b) drying and curing of the pasted grid, and c) electrochemical formation of the cured grid to produce the active materials used in the charged lead-acid battery. Battery formation is usually carried out by passing current through the electrode, which results in a positive plate having pellets of lead dioxide, and a negative plate having pellets of metallic lead. Tetrabasic lead sulfate, $4\text{PbO} \cdot \text{PbSO}_4$, is a very useful starting material for the preparation of positive electrodes for lead-acid batteries. According to U.S. Pat. No. 3,765,943 and U.S. Pat. No. 3,899,349, battery plates or electrodes fabricated with this sulfate and cured in the presence of a controlled amount of carbon dioxide gas, are associated with an increased product yield, greater life, greater reproducibility in the chemical and physical properties of the product, and crystal morphology more suitable for battery operation. Although both positive and negative electrodes may be formed with tetrabasic lead sulfate, this material is preferably used for positive plates. See

also Pavlov, D. and Papazov, G., Journal of Applied Electrochemistry 6, 1976, pp. 339-345, as well as Pavlov, D. and Kapkov, N.J., Electrochemical Society 137(1), 1990, pp. 16-28.

[0004] In the manufacturing process of lead-acid batteries, tetrabasic lead sulfate is usually produced by mixing the required amounts of leady oxide (α and β -PbO with free lead), sulfuric acid and water. Although this procedure seems to be very straightforward, several important variations of it have been reported, mainly in the patent literature.

[0005] For instance, U.S. Pat. No. 3,765,943 discloses a process for fabrication of positive electrodes for lead-acid batteries wherein the electrodes are fabricated from grids filled with paste and including the steps of reacting orthorhombic lead oxide in an aqueous suspension with sulfuric acid at 80-100°C to produce tetrabasic lead sulfate. The lead-containing material contains at least 90 wt% of lead oxide, the aqueous suspension in which the reaction takes place is preacidified to a pH range of 1-3.5 prior to the addition of lead oxide and the tetrabasic lead sulfate is separated from the aqueous suspension within one hour after complete addition of the sulfuric acid.

[0006] U.S. Pat. No. 4,324,768 discloses a process for the preparation of water insoluble lead compounds having a composition represented by the general formula $n\text{PbO} \cdot \text{PbX}_2$, wherein X stands for an inorganic acid radical, x indicates the valency of the radical X and n is a number of from 0 to 5, which comprises reacting lead monoxide according to the wet method with an inorganic acid or organic acid in the presence of hydroxylamine under such conditions that the initial pH value of the reaction system is not higher than 7. The lead compound represented by the general formula may be an ortho-salt such as lead chromate or a basic salt such as tetrabasic lead sulfate ($4\text{PbO} \cdot \text{PbSO}_4$). Further, it may be a salt containing at least two acid radicals, such as lead silicosulfate.

[0007] U.S. Pat. No. 5,096,611 discloses a process for making a battery paste comprising an initial step of forming a paste mixture by reacting a lead oxide having a

low free lead content with sulfuric acid in an aqueous slurry, followed by dewatering of the partially reacted slurry to obtain the paste material. In one described embodiment, a slurry containing one or more basic lead sulfates suitable for use as the active material in lead-acid battery electrodes is formed in a continuously stirred tank reactor. The slurry is withdrawn from the reactor and fed to a belt press, which reduces the moisture content of the slurry to the desired level. Battery pastes produced according to that invention may be fed continuously to a paster for mass production of positive and negative battery plates from grids. This process can utilize a variety of lead oxides including Barton, leady and nonleady oxides of any crystal structure, and can produce a paste containing either tribasic lead sulfate, tetrabasic lead sulfate, or a mixture thereof at a specified ratio. The amount of tetrabasic lead sulfate in the battery paste is determined during paste formation, and no subsequent adjustment is needed. Free lead can be removed or oxidized and the curing step is eliminated from the lead-acid battery manufacturing process. U.S. Pat. No. 5,290,359 discloses an apparatus for making a battery paste following the process disclosed in U.S. Pat. No. 5,096,611.

[0008] U.S. Pat. No. 5,252,105 discloses a continuous process in which an electrode for a lead-acid battery is prepared without the conventional curing step. The general procedure for preparing electrodes includes preparing a paste mixture comprising an active material precursor, sulfate-containing acids, and an inhibitor. The active material precursor includes lead oxides having at least 10% by weight lead oxide in the form of Pb_3O_4 (red lead), and a BET surface area of at least about $0.8 \text{ m}^2/\text{g}$; desirably about 1.00 to $1.50 \text{ m}^2/\text{grain}$ and preferably about 1.0 to $1.25 \text{ m}^2/\text{g}$. The inhibitor (preferably a simple sugar or a related compound having at least one hydroxyl group per carbon atom) prevents formation of tribasic lead sulfate and tetrabasic lead sulfate from the precursor material and sulfate-containing acids, except at elevated temperatures (tetrabasic lead sulfate forms with further processing at temperatures typically in excess of 80°C). The paste is applied to electrode grids and reacted at elevated temperatures for between about 5 and about 30 minutes, to form the active material of the electrode for both positive and negative electrodes. Plates

are then assembled into batteries and charged. Negative electrodes differ from the positive, mainly in the additives used.

[0009] U.S. Pat. No. 5,273,554 discloses a process for fabricating a battery in which tetrabasic lead sulfate is produced by reacting lead oxide with a substantial excess of a sulfate reactant at a pH in the range of 9.3 to 12. The resulting materials provide needle-like structures with a width generally in the range of 3 to 1 μm . The relative narrow needles, when employed on the positive electrode of a lead acid battery, improve the efficiency of formation, provide good adhesive to the positive plate, extend battery life, as well as, yield excellent capacity per gram of active material. In one embodiment, a precursor is prepared by reacting lead oxide with sulfuric acid in the presence of an excess of sulfate to form a paste and applying the paste to a grid with subsequent curing. Control of the temperature below 60°C in the reaction medium and of the sulfate excess yields, after curing at a temperature above 70°C and 100% humidity, a positive plate having an extremely uniform prismatic size, tetrabasic lead sulfate and a uniform pore distribution. Most significantly, the width of these crystals is extremely narrow – having an average dimension in the range of 1 to 2 μm – allowing rapid conversion to lead oxide from the precursor and further providing enhanced adhesion and current capacity attributes. Thus, the lead oxide obtained after conversion has prismatic crystals with an average crystal width less than 2.5 μm . In a second embodiment, tetrabasic lead sulfate of relative small prismatic size is achieved by just reacting lead oxide with sulfuric acid in a stirred aqueous solution containing excess sulfate at temperatures above 60°C to immediately form tetrabasic lead sulfate. The tetrabasic lead sulfate is mixed with water to form a paste. Positive plates made by applying this paste to a lead grid and converted to lead oxide, also have higher current capacity attributes. U.S. Pat No. 5,660,600 refers to the batteries fabricated according to the process disclosed in U.S. Pat. No. 5,273,554, as well as to the materials useful therein.

[0010] U.S. Pat. No. 6,454,977 discloses a continuous paste making process for lead-acid batteries that includes the steps of mixing water with a lead oxide, reacting an acid (usually sulfuric acid) with the lead oxide in a mixture to produce lead oxide-

lead sulfate compounds, and forming a paste comprising interlocking basic lead sulfate complex crystals from the lead lead-oxide sulfate compounds, where the mixing, reacting, and crystal forming steps occur in an extrusion or in a high-shear continuous processing apparatus. The method also includes the step of extruding the paste from the extrusion apparatus into a grid mesh where the paste is dried to form a battery plate of the lead-acid battery.

[0011] Evidently, tetrabasic lead-sulfate is an essential raw material for the lead-acid battery industry. Surprisingly, only a few synthesis methods, other than the ones mentioned above, have been reported in the scientific literature for the production of tetrabasic lead sulfate.

[0012] For instance, Burbank J., Journal of The Electrochemical Society 113(1), 1966, pp. 10-14, describes a method for the preparation of monobasic, tribasic and tetrabasic lead sulfates by reacting PbO and dilute sulfuric acid. The crystalline phases were identified by x-ray diffraction, and electron microscope examination showed all three to consist of prismatic needles. The three basic sulfates were pressed into pellets and oxidized anodically in a frame of pure lead and in 1.050 specific gravity sulfuric acid X-ray diffraction showed that each transformed to alpha lead dioxide. PbO₂ formed from pellets made from tetrabasic lead sulfate were mechanically strong formed by the interlocking of large crystals.

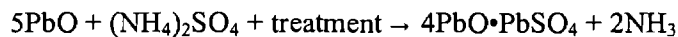
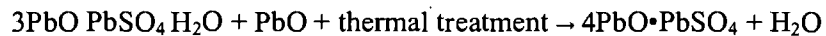
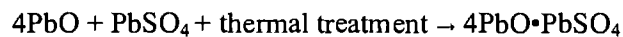
[0013] Vilhunen, Journal of Power Sources 39, 1992, pp.59, evaluated the differences arising on the positive active material with high tetrabasic lead sulfate content due to preparation technique or starting material. Wet chemical analysis, X-ray diffraction, transmission and scanning electron microscopy methods were used to characterize the materials. The tetrabasic lead sulfate was made from leady oxide and tetragonal PbO by solution or paste methods. The paste yielded smaller crystals which were also more irregular than the large single crystal-like particles resulting from the solution process. These results provide choices for achieving the crystal structure in conditional plates most conducive to long cycle life.

[0014] Lastly, Grugeondewaele et al., Journal of Power Sources 72(2), 1998, pp. 126-131, prepared tribasic lead sulfate and tetrabasic lead sulfate by reactive grinding. The effects of various experimental parameters (stoichiometry, hygrometry of the starting compounds, duration of mechanical treatment) upon the nature and morphological features of the resulting phase were investigated. With water in excess, only tribasic lead sulfate was produced while dry reagents led to tetrabasic lead sulfate. In both case, samples with a small particle size and high reactivity were obtained. In order to evaluate the influence of the morphology upon the electrochemical performances of such grinding produced samples, the capacity was measured and compared with that of traditional tribasic lead sulfate and tetrabasic lead-sulfate samples.

[0015] In brief, the available methods for the production of tetrabasic lead sulfate are complex, costly or yield heterogeneous crystal sizes.

SUMMARY

[0016] The present invention relates to different methods used in the production of tetrabasic lead sulfate by means of solid state reactions at high temperatures, which allow forming powdered sulfate compounds having a particle size of less than 10 μm . According to the present invention, the following reactions are employed to obtain the tetrabasic lead sulfate:



[0017] The procedures indicated in the present invention allow to obtain particles of tetrabasic lead sulfate having a size of less than 10 μm , avoiding any further milling

of the material and requiring only the employment of a dispersion process, which can be carried out either under dry conditions or in a liquid suspension.

[0018] In the methods which are claimed in the present invention, the chemical reaction that takes place between lead oxide and different sulfated compounds occurs in a single high temperature treatment.

[0019] Tetrabasic lead sulfate obtained according to the methods of the present invention can be used for the production of lead-acid battery pastes, the production of lead-acid battery plates made with said pastes, and the production of lead-acid batteries subsequently made with them.

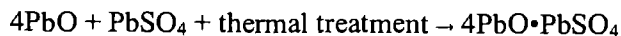
BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Fig. 1 shows a graph illustration of a characteristic x-ray diffraction pattern for tetrabasic lead sulfate obtained by a solid state reaction according to the present invention.

[0021] Fig. 2 shows a characteristic scanning electron microscopy micrograph of the tetrabasic lead sulfate obtained by a solid state reaction according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0022] The present invention relates to different methods used in the production of tetrabasic lead sulfate by means of solid state reactions at high temperatures, which allow forming powdered sulfate compounds having a particle size of less than 10 μm . According to the present invention, the following methods are employed to obtain the tetrabasic lead sulfate.



[0023] In this case, a solid state reaction method is proposed for the production of tetrabasic lead sulfate by reacting 4PbO and PbSO₄. This method comprising the steps

of mixing of the stoichiometric mixture of 4PbO and PbSO₄, heating the stoichiometric mixture of 4PbO and PbSO₄ at a temperature between 500 and 700°C during 3 to 8 hours and finally deagglomerating and sieving the resulting tetrabasic lead sulfate.

Example 1

[0024] Five mole of lead oxide were intimately mixed up with four mole of lead sulfate. A heat treatment of the reacting mixture at 600°C for 4 hours made it possible to achieve a degree of transformation of 95%.



[0025] In this case a solid state reaction method is proposed for the production of tetrabasic lead sulfate by reacting 3PbO•PbSO₄•H₂O + PbO. This method comprising the steps of mixing of the stoichiometric mixture of 3PbO•PbSO₄•H₂O + PbO, heating the stoichiometric mixture of 3PbO•PbSO₄•H₂O + PbO at a temperature between 500 and 700°C during 3 to 8 hours and finally deagglomerating and sieving the resulting tetrabasic lead sulfate.

Example 2

[0026] A degree of transformation into tetrabasic lead sulfate of 83.4% was achieved by heat treating at 600°C for 5 hours a mixture of one mole of tribasic lead sulfate with one mole of lead oxide.

[0027] An alternative method to this chemical route to produce tetrabasic lead sulfate is as follows:

[0028] Either by using active materials coming from the pastes used for the preparation of the lead-acid battery plates, or coming from recycled lead-acid battery plates. In this case, a solid state reaction method is proposed for the production of tetrabasic lead sulfate by reacting 3PbO•PbSO₄•H₂O + PbO. This method comprises the steps of mixing either the paste used for the preparation of the lead-acid battery plates, or the paste recovered from recycled lead-acid battery plates, heating the

mixture at a temperature between 500 and 700°C during 3 to 8 hours, and finally deagglomerating and sieving the resulting tetrabasic lead sulfate.

Example 3

[0029] A degree of transformation into tetrabasic lead sulfate of 93% was achieved by heat treating at 650°C for 5 hours the active materials coming from recycled lead-acid battery plates.



[0030] In this case a solid state reaction method is proposed for the production of tetrabasic lead sulfate by reacting $5\text{PbO} + \text{H}_2\text{SO}_4$. This method comprising the steps of mixing the PbO with 1 mole of a H_2SO_4 aqueous solutions having a specific gravity in the range of 1.100 to 1.400 g/cm^3 , following this by a temperature rise of the stoichiometric mixture to 500 – 700°C, holding the mixture at that temperature for 3 to 8 hours, and finally deagglomerating and sieving the resulting tetrabasic lead sulfate.

Example 4

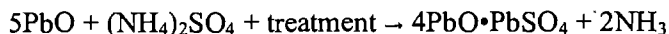
[0031] A degree of transformation into tetrabasic lead sulfate of 72.9% was achieved by heat treating at 600°C for 6 hours a mixture of 5 mole of PbO with 1 mole of a H_2SO_4 aqueous solution having a specific gravity of 1.150 g/cm^3 .



[0032] In this case, a solid state reaction method is proposed for the production of tetrabasic lead sulfate by reacting $4\text{PbO} + \text{PbCO}_3 + \text{H}_2\text{SO}_4$, comprising the steps of mixing a stoichiometric mixture of $4\text{PbO} + \text{PbCO}_3$, followed by the addition of 1 mole of a H_2SO_4 aqueous solution having a specific gravity in the range of 1.100 to 1.400 g/cm^3 , then heating the stoichiometric mixture of $4\text{PbO} + \text{PbCO}_3 + \text{H}_2\text{SO}_4$ at a temperature between 500 and 700°C for 3 to 8 hours, and finally deagglomerating and sieving the resulting tetrabasic lead sulfate.

Example 5

[0033] A degree of transformation into tetrabasic lead sulfate of 85% was achieved by heat treating at 650°C for 6 hours a mixture of 4 mole de PbO with 1 mol of PbCO₃ plus 1 mole of a H₂SO₄ aqueous solution having a specific gravity of 1.150 g/cm³.



[0034] In this case, a solid state reaction method is proposed for the production of tetrabasic lead sulfate by reacting 5PbO + (NH₄)₂SO₄, comprising the steps of mixing the stoichiometric mixture of 5PbO + (NH₄)₂SO₄, then heating the stoichiometric mixture of 5PbO + (NH₄)₂SO₄ at a temperature between 500 and 700°C during 3 to 8 hours, and finally deagglomerating and sieving the resulting tetrabasic lead sulfate.

Example 6

[0035] A degree of transformation into tetrabasic: lead sulfate of 80% was achieved by heat treating at 650°C for 6 hours a mixture of 5 mole of PbO with 1 mol of (NH₄)₂SO₄.

[0036] The characteristic X-ray diffraction angles for the tetrabasis lead sulfate obtained according to the present invention are shown in the following table and the corresponding peak intensities are indicated in Fig. 1.

X-Ray Diffraction Angle	Corresponding Phase (4BS = tetrabasic lead sulfate)
10.70	4BS
27.60	4BS
28.70	4BS
29.20	4BS
31.00	4BS
33.60	4BS
46.00	4BS
46.50	4BS

[0037] The morphology and size of the particles obtained according to the present invention can be observed in Fig. 2. Procedures indicated in the present invention allow to obtain particles of tetrabasic lead sulfate having a size of less than 10 μm , avoiding any further milling of the material and requiring only the employment of a dispersion process, which can be carried out either under dry conditions or in a liquid suspension.

[0038] The production of tetrabasic lead sulfate by using a wet procedure involves the formation of tribasic lead sulfate intermediate compound, which must be transformed later into tetrabasic lead sulfate by means of a suitable heat treatment. In contrast, in the methods which are claimed in the present invention, the chemical reaction that takes place between lead oxide and different sulfated compounds occurs in a single high temperature treatment.

[0039] Tetrabasic lead sulfate obtained according to the methods of the present invention can be used for the production of lead-acid battery pastes, the production of lead-acid battery plates made with said pastes, and the production of lead-acid batteries subsequently made with them.

WHAT IS CLAIMED IS:

- 1 1. A solid state reaction method for the production of tetrabasic lead
2 sulfate by reacting 4PbO and PbSO_4 , comprising the steps of:
3 mixing a stoichiometric mixture of 4PbO and PbSO_4 ;
4 heating the stoichiometric mixture of 4PbO and PbSO_4 at a
5 temperature between 500 and 700°C for 3 to 8 hours; and
6 deagglomerating and sieving resulting tetrabasic lead sulfate.
- 1 2. A solid state reaction method for the production of tetrabasic lead
2 sulfate by reacting $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} + \text{PbO}$, comprising the steps of:
3 mixing a stoichiometric mixture of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} + \text{PbO}$;
4 heating the stoichiometric mixture of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} + \text{PbO}$ at a
5 temperature between 500 and 700°C for 3 to 8 hours; and
6 deagglomerating and sieving resulting tetrabasic lead sulfate.
- 1 3. A solid state reaction method according to Claim 2 wherein said
2 mixture of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} + \text{PbO}$ is obtained from active materials coming from
3 pastes used for the preparation of the lead-acid battery plates, or coming from
4 recycled lead-acid battery plates.
- 1 4. A solid state reaction method for the production of tetrabasic lead
2 sulfate by reacting $5\text{PbO} + \text{H}_2\text{SO}_4$, comprising the steps of:
3 mixing a stoichiometric mixture of $5\text{PbO} + \text{H}_2\text{SO}_4$;
4 heating the stoichiometric mixture of $5\text{PbO} + \text{H}_2\text{SO}_4$ at a temperature
5 between 500 and 700°C for 3 to 8 hours; and
6 deagglomerating and sieving resulting tetrabasic lead sulfate.
- 1 5. A solid state reaction method for the production of tetrabasic lead
2 sulfate by reacting $4\text{PbO} + \text{PbCO}_3 + \text{H}_2\text{SO}_4$, comprising the steps of:
3 mixing a stoichiometric mixture of $4\text{PbO} + \text{PbCO}_3 + \text{H}_2\text{SO}_4$;
4 heating the stoichiometric mixture of $4\text{PbO} + \text{PbCO}_3 + \text{H}_2\text{SO}_4$ at a
5 temperature between 500 and 700°C for 3 to 8 hours; and

6 deagglomerating and sieving resulting tetrabasic lead sulfate.

1 6. A solid state reaction method for the production of tetrabasic lead
2 sulfate by reacting 5PbO -/- $(\text{NH}_4)_2\text{SO}_4$, comprising the steps of:
3 mixing a stoichiometric mixture of 5PbO -/- $(\text{NH}_4)_2\text{SO}_4$;
4 heating the stoichiometric mixture of 5PbO -/- $(\text{NH}_4)_2\text{SO}_4$ at a
5 temperature between 500 and 700°C for 3 to 8 hours; and
6 deagglomerating and sieving resulting tetrabasic lead sulfate.

1 7. A lead-acid battery paste comprised of the tetrabasic lead sulfate
2 obtained according to the method of Claim 1.

1 8. A lead-acid battery paste comprised of the tetrabasic lead sulfate
2 obtained according to the method of Claim 2.

1 9. A lead-acid battery paste comprised of the tetrabasic lead sulfate
2 obtained according to the method of Claim 3.

1 10. A lead-acid battery paste comprised of the tetrabasic lead sulfate
2 obtained according to the method of Claim 4.

1 11. A lead-acid battery paste comprised of the tetrabasic lead sulfate
2 obtained according to the method of Claim 5.

1 12. A lead-acid battery paste comprised of the tetrabasic lead sulfate
2 obtained according to the method of Claim 6.

1 13. The solid state reaction method of Claim 1 wherein the step of heating
2 the stoichiometric mixture of 4PbO and PbSO_4 is performed at a temperature of
3 approximately 600°C .

1 14. The solid state reaction method of Claim 13 wherein the step of
2 heating the stoichiometric mixture of 4PbO and PbSO_4 is performed for
3 approximately 4 hours.

- 1 15. The solid state reaction method of Claim 1 wherein the tetrabasic lead
2 sulfate has a particle size of less than 10 μm .
- 1 16. The solid state reaction method of Claim 1 wherein the step of
2 deagglomerating and sieving is a dispersion process.
- 1 17. The solid state reaction method of Claim 16 wherein the dispersion
2 process is carried out under dry conditions.
- 1 18. The solid state reaction method of Claim 16 wherein the dispersion
2 process is carried out in a liquid suspension.
- 1 19. A method of forming a battery plate comprising:
2 mixing a stoichiometric mixture of 4PbO and PbSO_4 ;
3 heating the stoichiometric mixture of 4PbO and PbSO_4 at a
4 temperature between approximately 500 and 700°C for between approximately 3 and
5 8 hours to form tetrabasic lead sulfate;
6 deagglomerating and sieving the tetrabasic lead sulfate;
7 forming a paste using the tetrabasic lead sulfate; and
8 providing the paste on a battery plate.
- 1 20. The method of Claim 19 wherein the step of heating the stoichiometric
2 mixture of 4PbO and PbSO_4 is performed at a temperature of approximately 600°C.
- 1 21. The method of Claim 20 wherein the step of heating the stoichiometric
2 mixture of 4PbO and PbSO_4 is performed for approximately 4 hours.
- 1 22. The method of Claim 19 wherein the tetrabasic lead sulfate has a
2 particle size of less than 10 μm .
- 1 23. The method of Claim 19 wherein the step of deagglomerating and
2 sieving is a dispersion process.
- 1 24. The method of Claim 23 wherein the dispersion process is carried out
2 under dry conditions.

1 25. The method of Claim 23 wherein the dispersion process is carried out
2 in a liquid suspension.

1 26. A lead-acid battery produced by a method comprising:
2 providing a battery comprising a plurality of battery plates, the battery
3 plates prepared by a method comprising:
4 mixing a stoichiometric mixture of 4PbO and PbSO_4 ;
5 heating the stoichiometric mixture at a temperature between
6 500 and 700°C for a period of between approximately 3 and 8 hours to form
7 tetrabasic lead sulfate;
8 deagglomerating and sieving the tetrabasic lead sulfate;
9 forming a paste using the deagglomerated and sieved tetrabasic
10 lead sulfate; and
11 providing the paste on a battery plate.

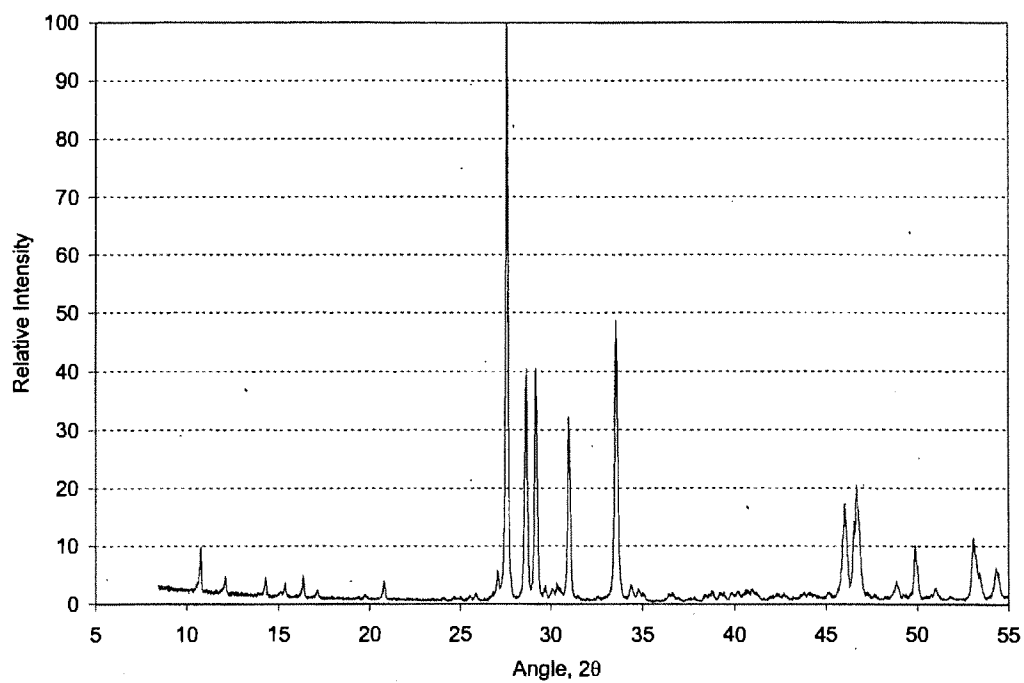
1 27. The lead-acid battery of Claim 26 wherein the step of heating the
2 stoichiometric mixture is performed at a temperature of approximately 600°C .

1 28. The lead-acid battery of Claim 26 wherein the step of heating the
2 stoichiometric mixture is performed for approximately 4 hours.

1 29. The lead-acid battery of Claim 26 wherein the tetrabasic lead sulfate
2 has a particle size of less than $10\text{ }\mu\text{m}$.

1 30. The lead-acid battery of Claim 29 wherein the step of heating the
2 stoichiometric mixture is performed at a temperature of approximately 600°C for
3 approximately 4 hours.

1/2

**Fig 1**

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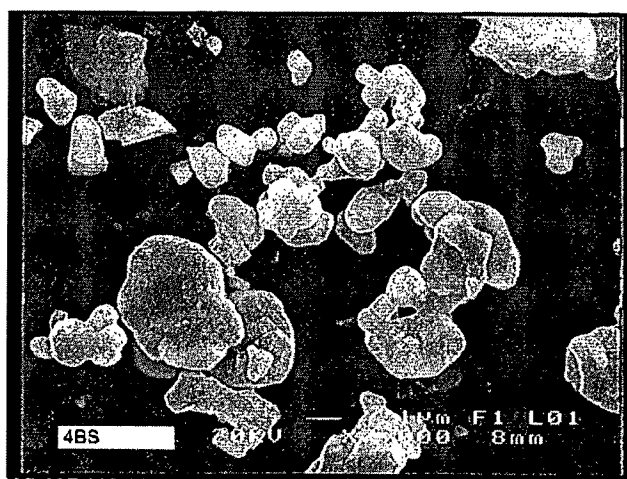


Fig. 2

INTERNATIONAL SEARCH REPORT

IB2005/002373

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01G21/20 H01M4/56 H01M10/12 H01M4/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01G H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, INSPEC, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GRUGEON-DEWAELE S ET AL: "Synthesis and electrochemical preformances of tribasic and tetrabasic lead sulfates prepared by reactive grinding" JOURNAL OF POWER SOURCES, ELSEVIER, AMSTERDAM, NL, vol. 72, no. 2, 21 April 1998 (1998-04-21), pages 126-131, XP004124821 ISSN: 0378-7753 cited in the application pages 126-129	1-30
X	----- EP 0 540 229 A (AMERICAN TELEPHONE AND TELEGRAPH COMPANY; AT&T CORP) 5 May 1993 (1993-05-05) examples 1,2	7-12, 26-30
A	----- ----- -/-	1-6, 13-25

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- *&* document member of the same patent family

Date of the actual completion of the international search

17 October 2005

Date of mailing of the international search report

24/10/2005

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 336 236 A (KOLAKOWSKI ET AL) 22 June 1982 (1982-06-22) column 5, lines 57-64 -----	1-6

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			JP	3328332 B2	24-09-2002
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US 4336236	A	22-06-1982	BE	892628 A1	16-07-1982
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